

(54) TITLE OF THE INVENTION: Method of manufacturing carbon single layer nanotube

(57) ABSTRACT

PROBLEM:

It has been impossible to keep manufacturing of carbon single layer nanotube of high quality for a long time.

SOLVING MEANS:

High frequency plasma without electrode, if used, would not in principle generate such a change in plasmatic state as caused by wear of electrode under arc discharge method and enable carbon single layer nanotube to be stably synthesized for a long time.

Supply of hydrogen gas etching carbon and argon gas cooling quickly gas temperature to periphery of high frequency plasma, executed separately from supply of raw material, permits generation of impurities, including amorphous carbon and graphite, to be suppressed without reduction in yielding of the carbon single layer nanotube.

WHAT Is Claimed Is:

1. A method of manufacturing carbon single layer nanotube characterized by supply of carbon material and metallic catalyst into plasma already generated by using high frequency plasma without electrode.
2. A method of manufacturing carbon single layer nanotube characterized by supplying separately each of carbon material and metallic catalyst into plasma already generated by using high frequency plasma without electrode.
3. A method of manufacturing carbon single layer nanotube, according to Claim 1 or 2, wherein hydrocarbon gas is used as carbon

material.

4. A method of manufacturing carbon single layer nanotube, according to Claim 1 or 2, wherein particulate metallic catalyst is supplied into plasma.
5. A method of manufacturing carbon single layer nanotube, according to Claim 1, wherein organic metal is used as carbon material and metallic catalyst.
6. A method of manufacturing carbon single layer nanotube, according to Claim 1 or 2 or Claim 3 or 4 or Claim 5, wherein gas etching carbon is supplied into plasma.
7. A method of manufacturing carbon single layer nanotube, according to Claim 1 or 2 or Claim 3 or 4 or Claim 5, wherein temperature in area of plasma is locally lowered.
8. A method of manufacturing carbon nanotube, according to Claim 1 or 2 or Claim 3 or 4, Claim 5 or 6 or Claim 7, wherein base of collecting carbon nanotube is cooled.

DETAILED DESCRIPTION OF THE INVENTION:

[0001] TECHNICAL FIELD OF THE INVENTION:

The present invention relates to the method of manufacturing the carbon single layer nanotube, and more specifically to the method of manufacturing the carbon single layer nanotube, wherein long time's and continuous manufacturing thereof is possible.

[0002] PRIOR ART:

The carbon nanotube comprises one unit of or a couple telescopic units of cylinder(s), which are made by rounding face of graphitic carbon atom, a couple of atomic layers thick and is extremely microscopic matter being in order of nm for outer diameter.

[0003]

There have been marked scatters for electric properties and chemical properties of ordinary carbon nanotube, wherein a plurality of cylindrical graphite layers are concentrically formed. From that view the carbon single layer nanotube, getting shape of the tube controlled into single layer, has been developed.

[0004]

For method of manufacturing the carbon single layer nanotube, conventionally, the arc discharge, using carbon rod as electrode, has been adopted. Because this technique synthesizes the carbon nanotube with carbon material of electrode used as raw material, consumption of the electrode is unavoidable along with lapse of manufacturing time, a state of the arc discharge, by itself, being changed as time goes by.

[0005]

To synthesize highly efficiently the carbon single layer nanotube, there is necessity of metallic catalyst such as iron and nickel in addition to carbon as raw material. In the arc discharge method wherein the metal as catalyst is often supplied in a form of burying the metal into the carbon electrode, when temperature of electrode gets higher at discharge, the metal as catalyst, higher in vapor pressure in comparison with carbon, evaporates earlier than the carbon, so ratio of supplying quantity between the carbon and catalyst is changed as time goes by.

[0006]

For the above — mentioned reason the arc discharge method cannot hope stableness in manufacturing constancy in case where the manufacturing process is as long as over a couple of minutes and incurs difficulty in keeping to synthesize the carbon single nanotube for a long time.

[0007] PROBLEM TO BE SOLVED BY THE INVENTION:

The carbon single layer nanotube could become stiff carbon fibers

because of being better for crystallizability. But the conventional arc discharge device cannot be run for a long time over a couple of minutes not only due to consumption of carbon electrode but because ratio of supplying quantity between the carbon and the catalyst is changed as time goes by, resulting in difficulties in getting yield of the carbon single layer nanotube to extent satisfactory enough to be offered for practical use.

[0008]

For this reason in proportion to industrial development involved in carbon single layer nanotube it becomes more unavoidable task that synthesizing method capable of executing long time's running is established.

[0009]

A further task lies in suppression of amorphous carbon and graphite, both of which are generated at synthesization of the carbon single layer nanotube, thereby obtaining manufacturing conditions of getting carbon single layer nanotube of high quality.

[0010] MEANS OF SOLVING PROBLEMS:

To solve the above — mentioned problem, due to necessity of generating high temperature plasma without use of the carbon electrode in direct contact to the plasma, the present invention permits the high frequency coil to generate the plasma without electrode.

[0011]

This method enables stabilization of shape of plasma by controlling gas stream to provide plasma noncontact to any wall face and allows introduction of the method into synthesization of the carbon single layer nanotube to reduce limit to the synthesizing time appropriately to nil.

[0012]

It is preferable to use gas, favorable for controllability of quantity of being supplied, as carbon material, available scope of the used gas

including hydrocarbon such as methane and so on.

[0013]

If the metallic catalyst is supplied into the plasma fully separately from the carbon resource, ratio of supplying quantity between the carbon and the metallic catalyst is not changed, even if time goes by.

[0014]

To suppress the amorphous gas and graphite, which are generated at formation of the carbon single layer nanotube, an addition of hydrogen or oxygen, having action of etching the carbon, would meet requirements. A supply of gas into some portion of plasma from outside would lower quickly temperature of the plasma to cool promptly generated powder, also whereby formation of side formed matter such as amorphous carbon and graphite can be suppressed.

[0015]

Furthermore, cooling of base for collecting the carbon single layer nanotube in a water-cooled manner suppresses generation of multi-layer carbon nanotube, enabling single layer carbon nanotube to be selectively manufactured.

[0016]

FORM OF THE PREFERRED EMBODIMENT OF THE INVENTION:

The following part contains description of one form of the embodiment of the present invention :

[0017]

Because the method of manufacturing the carbon single layer nanotube according to the present invention uses the high frequency plasma without electrode, such a problem of wear of electrode as found in the arc discharge is not in principle incurred, enabling long time's running to be executed.

[0018]

To avoid generation of timewise scatter of quality of the generated matter at manufacturing thereof, a satisfactory process lies simply in constant supply of constant quantity of the carbon material and metallic material in use for catalyst into the plasma. For that purpose the metal in use for the catalyst is supplied in a form of powder, while being put on constant flow

of carrier gas, whereas the hydrocarbon gas is supplied in form of the hydrocarbon gas, whose flow rate is controlled, in a manner of being separated from the supply of the metal in use for the catalyst.

[0019]

According to the preferred embodiment of the present invention, the plasma in arc area is generated usually at a couple of hundreds Torr for vacuum degree. In that case temperature of atom in the plasma reaches high temperature of 10 thousand °C and supplied metallic particles in use for catalyst, couples of μm for particle diameter, are approximately fully evaporated. The hydrocarbon gas in use for the carbon material is transformed into atom in the plasma with ease.

[0020]

The carbon being transformed into atom in the plasma and the metal in use for catalyst gather at part of lower temperature located in periphery of the plasma flame to form fine particles. A catalytic action on the fine particles permits the carbon atom, of solid solution, or flying carbon atom to form the carbon single layer nanotube.

[0021]

At that time, however, the amorphous carbon and the graphite are formed and because the carbon single layer nanotube is higher for growth speed, an addition of hydrogen or oxygen, etching the carbon, could make etching of the amorphous carbon and the graphite earlier, thereby obtaining the carbon single layer nanotube superior in quality.

[0022]

The gas is supplied from outside into the periphery of plasma flame, where the fine particles are formed and temperature of the plasma is quickly lowered to stop reaction between the amorphous carbon and the graphite, both of which are slower for growth speed, before the amorphous carbon and the graphite have not yet been fully formed, thereby enabling the carbon single nanotube superior of quality to be obtained.

[0023]

Furthermore, cooling of the base for collecting the carbon single

layer nanotube in a water-cooled manner would suppress generation of multi-layer carbon nanotube and enable the single-layer carbon nanotube to be selectively manufactured.

[0024] EMBODIMENTS:

EMBODIMENT 1:

The following description of the embodiments according to the present invention is made in conjunction with FIGURE 1:

[0025]

According to the present embodiment a supply of electric power, about 10k W at 4 MHz for oscillating frequency, into coil 3 in high frequency plasma generating device can form the high temperature plasma 2 with size of couples of cm at about 300 Torr for vacuum degree.

[0026]

To stabilize shape of the plasma, about 60 liter per minute of argon gas is supplied from above part of FIGURE and formed powder which is generated in the plasma, reaches the cooled base 4, while being put on flow of the argon gas, subsequently the formed powder being collected.

[0027]

According to the present embodiment, a necessity of the metallic catalyst for synthesization of the carbon single layer nanotube gets the metal in use for catalyst transported in a form of powder, about 3~5 μ m for powder diameter, through nozzle 1 up to the plasma at volume rate of 3 liter per minute by using flow type powder supply unit, while putting the metal in use for catalyst on flow of carrier gas of argon.

[0028]

In the case where the flow quantity of the carrier gas is smaller than 1 liter per minute, because gas flow, in a reverse direction, which exists in plasma, does not cause the powder to be supplied to center

of the plasma, resulting in insufficient evaporation of the metal in use for catalyst, the present embodiment sets the flow rate of the argon carrier gas to 3 liter per minute.

[0029]

With any of iron, cobalt and nickel which are contained in any of kinds of the metal in use for catalyst, it is possible to synthesize the carbon single layer nanotube. A using of mixture powder comprising nickel (75%) and cobalt (25%), makes substantially yield rate of carbon single layer nanotube highest. Standard supply quantity of metallic powder is about 100mg per minute.

[0030]

The methane as carbon source is supplied into periphery on downstream side of the plasma flame at rate of about 1 liter per minute. Even if the side of upper stream of the plasma flame is selected as place into which the methane is supplied, it does not practically incur any problem, because no damage is given to the stability of the plasma, providing that supply quantity thereof is about 1 liter per minute.

[0031]

To suppress generation of the amorphous carbon and the graphite, which are formed together with the carbon single layer nanotube, hydrogen having etching action to the carbon, is supplied into the downstream side of the plasma at the supply rate of 6 liter per minute. Because if ratio of supply quantity of the hydrogen to supply quantity of the methane is 2 or 3, a great amount of amorphous carbon and graphite is generated around metallic fine particles in use for catalyst, the present embodiment makes a selection of ratio of supply quantity of hydrogen to exceed 5.

[0032]

The above-mentioned method causes fine particles, much more than the plasma flame, to be discharged in a sooty state. Confirmation by electronic microscope shows that the fine particles contain a great amount of carbon single layer nanotube. If the fine particles are collected on base, exposed to the plasma flame, which is located at

high temperature of about 1000°C, instead of the carbon single layer nanotube, many multi-layer carbon nanotubes partially comprising 2 or 3 layers, are found and the carbon nanotube is checked to be grown up in a diametral direction on the base. For this reason, to obtain the single layer nanotube only, it is preferable to make collection on the base cooled in a water-cooling manner.

[0033] EMBODIMENT 2:

To suppress generation of the amorphous carbon and the graphite, the argon gas is supplied in downstream side of the plasma at supply rate of 15 liter per minute. The argon gas by itself has no action of etching the carbon and a quick cooling of the plasma following the introduction of argon gas permits priority to be given to the carbon single layer nanotube being higher for growth speed so that the carbon single layer nanotube may remain at first and enables the generation of other amorphous carbon and graphite to be suppressed.

[0034]

A visual inspection checks also the cooling phenomenon from lowering of radiational strength of the downstream side of plasma at the time of introducing the argon gas. In comparison with case of making no introduction of argon, the executed introduction thereof might reduce the amorphous carbon and graphite which exist around metallic particles in use for catalyst, especially marked reduction of the graphite getting conspicuous. That may be considered to be caused by improvement in crystallizability of the amorphous carbon at high temperature to hinder process of becoming graphite with quick cooling of the gas.

[0035]

On the other hand an observation of crystallizability of the carbon single layer nanotube by the electronic microscope checks that the gas cooling method gives no worse influence to the crystallizability thereof.

[0036] EMBODIMENT 3:

Due to wide scatter in particle diameter of metallic powder, obtainable

at market with ease, with the metallic powder used as raw material for the metal in use for the catalyst, before the metallic powder being larger for particle diameter is fully evaporated in the plasma, a collection of mixture between the formed matter and the metallic powder may be sometimes made.

[0037]

To prevent such a problem, organic metal is used as metallic catalyst source. The present embodiment uses ferrocene which is organic metal of the iron. Because the ferrocene is as low as 140°C for sublimation temperature, it is fully evaporated in the plasma and such raw material powder, not yet decomposed, as found at use of the metallic powder, do not get mixed.

[0038]

A use of the ferrocene as raw material for catalyst along with a use of methane as raw material for carbon makes it possible to synthesize highly efficiently the carbon single layer nanotube.

[0039]

A construction of getting carbon atom contained in the ferrocene could synthesize the carbon single layer nanotube, using only the ferrocene without use of the methane, although the yield rate thereof is relatively lower.

[0040] EFFECT OF THE INVENTION:

The conventional method, adopting the arc discharge, of manufacturing the carbon single layer nanotube has consumed not only carbon as electrode at discharge but also rapidly the metal in use for catalyst, buried in the electrode, due to its higher vapor pressure. Wear of the carbon electrode incurs change in state of plasma as time goes by and a selective evaporation of metal in use for catalyst changes supply volume of the carbon and the metal in use for the catalyst into the plasma, whereby difficulties are brought to the long time's synthesization of the carbon single layer nanotube.

[0041]

To solve this problem, the present invention uses device for synthesizing plasma without electrode as shown in FIGURE 1. The device is to form the plasma, whose highest temperature reaches about 10 thousand °C, without contact to any side face, by means of high frequency coil, 4 MHz. As a result the synthesization of the carbon single layer nanotube without time limit gets possible.

[0042]

While the metal in use for the catalyst is supplied in a form of powder having couples of μm of particle diameter during course of being put on constant carrier gas stream, the carbon material, as methane gas, is supplied stably by way of gas flow meter into the plasma. If supply of each of the metallic catalyst and the carbon to the plasma takes a separately independent supply system, ratio of supply quantity of each component element is constant and the carbon single layer nanotubes being the same for quality can be synthesized.

[0043]

At the same time when the carbon and the metal in use for catalyst, which are transformed into atom in the plasma, gather in low temperature part of periphery of the plasma to generate formed powder, the amorphous gas and graphite are also generated. From that view the present invention utilizes features of carbon single layer nanotube, wherein it is higher for growth speed than other phases, and an addition of the hydrogen and the oxygen, both of which etch the carbon, is made, whereby the amorphous carbon and the graphite are etched earlier to enable the carbon single layer nanotube superior of quality to be obtained.

[0044]

Other technique aiming at the same effect supplies the argon gas from outside into periphery of the plasma to lower quickly the temperature of plasma to cause quick cooling to stop the reaction at the stage of forming still insufficiently the amorphous carbon and the graphite both of which is slower for growth speed so that the carbon single layer nanotube superior of quality can be obtained.

[0045]

A use of cooled collecting base could suppress generation of carbon nanotube comprising a plurality of layers and obtain selectively the single layer carbon nanotube.

BRIEF DESCRIPTION OF THE DRAWING:

FIGURE 1 is a conceptual view of a device for manufacturing carbon single layer nanotube with high frequency plasma used according to the present invention.

DESCRIPTION OF NUMERAL SYMBOLS:

1. Powder supply port.
2. Plasma.
3. High frequency coil.
4. Collecting base.